H-USY zeolites as heterogeneous catalysts for Friedel-Crafts reactions: reaction study and modelling of toluene acylation and bromobenzene alkylation.

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Two Friedel-Crafts reactions are studied, whereby a solid zeolite catalyst is used instead of the traditional polluting liquid acids normally used for these reactions. Zeolite catalysts have already proven their worth in several large industrial Friedel-Crafts processes, but the full potential of these zeolites has not yet been achieved in the fine chemicals industry. The reactions studied in this work include alkylation and acylation of a poorly activated and a deactivated aromatic substrate.

The selected Friedel-Crafts reactions are the acetylation of toluene with acetic anhydride and the alkylation of bromobenzene with allyl acetate with zeolite H-USY as catalyst. The Friedel-Crafts acylation reaction of toluene with acetic anhydride produces *para*-methylacetophenone, a compound that has applications in perfumery, flavours and fragrance industry. The Friedel-Crafts alkylation reaction of bromobenzene with allyl acetate produces a molecule with interesting functionalities which is very attractive for further functionalization to fine chemicals.

To study these reactions a high-throughput continuous flow reaction setup is used. A reaction study is performed by varying several reaction conditions. The insights gained during the reaction study are implemented into an adsorption/reaction model. The equations in this model include the adsorption and chemical reaction of the compounds on the zeolite, and the deactivation of the zeolitic catalyst. The modelling work was used to confirm or eliminate certain reaction mechanisms, and to find the most plausible reaction scheme for the studied acylation or alkylation reaction.

Zeolite H-USY was found to be an active catalyst for both Friedel-Crafts reactions studied in this work. For the acylation reaction of toluene with acetic anhydride, the main reaction products formed at all times are methylacetophenone and its expected side product acetic acid. The production of the desired reaction product *para*-methylacetophenone is very selective compared to the other methylacetophenone isomers. By decreasing the contact time, consecutive (undesired) reactions from methylacetophenone are avoided. This is coupled with a slower deactivation, which

strongly favours the idea that deactivation is caused by a series of consecutive reactions. These consecutive reactions form large molecules which block the internal volume of the zeolite, thus preventing access to the zeolite sites.

For the alkylation reaction of bromobenzene with allyl acetate (deactivated aromatic and bifunctional agent), alkylated product made up 50% of the product stream at all times with acetic acid as expected side product. The primary alkylation product, allyl bromobenzene, rapidly isomerizes to *cis-* and *trans*-propenylbromobenzene. All of these products are interesting as building blocks in further functionalisation. The distribution among the alkylated products depends on the deactivation degree of the zeolite. The reaction conditions can thus be tuned according to the most desired reaction product.

Deactivation for this reaction is caused by the oligomerisation of the allylic function of allyl acetate. As this reaction runs in parallel with the desired reaction, it is very hard to avoid this reaction. The most optimal conditions in order to minimize side reaction, the H-USY catalyst should be used at relatively low temperature and low concentration of allyl acetate in the feed.

A large part of this research was devoted to modelling the behaviour of the zeolite in plug flow reactors in order to describe the whole process taking place over the zeolite. Besides the equations describing the plug flow reactor, the model included several important phenomena related to chemical reactions on zeolites: adsorption, reaction and deactivation. Through this approach, the modelling for the acetylation reaction of toluene with acetic anhydride was successful. The model correctly describes the concentration profiles of all reaction products in function of TOS, the product distribution of the methyl acetophenone isomers and of course the deactivation. For the alkylation reaction of bromobenzene with allyl acetate, this approach allowed the correct prediction of the alkylated product distribution and the deactivation of the catalyst. The model also included some side reactions. Unfortunately, an important side reaction could not be described properly.

In general, this research has demonstrated the merits and limitations of an approach based on high throughput reaction studies and the application of an adsorption/reaction model.